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THE OXIDATION NUMBER OF ANTIMONY IN ANTIMONY PENTASULFIDE

G. G. Long, J. G. Stevens and L. H. Bowen

Department of Chemistry, North Carolina State University, Raleigh, N. C. 27607

and

S. L. Ruby

Argonne National Laboratory, Argonne, Illinois

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The +3 and +5 oxidation states of antimony are well-defined by a variety of compounds, and thus, it is not surprising to find a trisulfide, Sb_2S_3, and a pentasulfide, Sb_2S_5, enumerated in lists of antimony compounds. Antimony(III) sulfide exists in two forms: a gray-black crystalline modification, stibnite, which consists of pairs of infinite antimony-sulfur chains (1), and an orange amorphous solid. The so-called pentasulfide, however, has a variable sulfur content and always contains a certain amount of loosely bound sulfur, which may be removed by extraction with carbon disulfide. An X-ray diffraction powder pattern has been reported for antimony pentasulfide (2), but in many instances this material seems to be essentially amorphous. Thus, there is considerable question as to the existence of Sb_2S_5 as a definite compound and a further question as to whether this material contains Sb(V). Since the Mössbauer isomer shift (I.S.) parameter is particularly sensitive to oxidation state, we have recorded ^{121}Sb Mössbauer spectra for $Sb_2S_{3(Stibnite)}$, $Sb_2S_{3(Amorph.)}$ and for two samples of Sb_2S_5 (hereafter identified as antimony pentasulfide$_{(I)}$ and antimony pentasulfide$_{(II)}$).

Sources and Characterization of Materials. All of the sulfides were purchased from common suppliers of laboratory chemicals (stibnite -- Fisher Scientific Co., Cat. No. A868; amorphous antimony trisulfide -- J. T. Baker Chemical Co.; antimony pentasulfide$_{(I)}$ -- Alfa Inorganics, Inc., Cat. No. SB-117;

antimony pentasulfide$_{(II)}$ -- E. H. Sargent and Co.). None of the sulfides were purified further, but they were characterized by (a) taking X-ray diffraction patterns and comparing them with the published powder patterns of stibnite (3) and of antimony pentasulfide (2), and (b) quantitatively determining antimony and free sulfur.

Antimony was determined by a permanganate titration (4). Free sulfur was determined in the amorphous trisulfide and in the two pentasulfides by extraction of weighed samples in a Soxhlet extractor for one day with CS_2. The residue was dried, weighed and then extracted again for a day to insure that all free sulfur had been extracted. The samples of amorphous antimony trisulfide and of antimony pentasulfide$_{(I)}$ attained constant weight after the 1-day extraction, but the sample of antimony pentasulfide$_{(II)}$ was still losing weight after 6 days extraction. A summary of the analytical data is given in Table I. Included is the percent antimony, the formula of the sample based on the antimony determination, the percent weight loss, and the formula of the residue arrived at by correcting the sample formula by the number of gram-atoms of free sulfur.

TABLE I

Summary of Analytical Data for the Antimony Sulfides

Antimony Sulfide	% Sb	Formula (Sb_2S_n) for the Sample	% Weight Loss	Formula (Sb_2S_n) for the Residue
Stibnite	71.90	$Sb_2S_{2.97}$	---	---------
Amorph. Antimony Trisulfide	68.14	$Sb_2S_{3.55}$	0.0	$Sb_2S_{3.55}$
Antimony Pentasulfide$_{(I)}$	63.20	$Sb_2S_{4.4}$	7.2	$Sb_2S_{4.0}$
Antimony Pentasulfide$_{(II)}$	23.84	$Sb_2S_{24.3}$	24.9*	$Sb_2S_{16.1}$*

*The residue was not at constant weight, but extraction was discontinued after 6 days.

The powder patterns were determined on a Philips Electronics X-ray Diffractometer using filtered Co K or Cu K radiation. The powder pattern for our sample of $Sb_2S_{3(Stibnite)}$ was identical to the published stibnite pattern (3);

the patterns for $Sb_2S_{3(Amorph.)}$ and antimony pentasulfide$_{(I)}$ showed essentially no diffraction peaks and therefore these samples are amorphous; the X-ray diffraction powder pattern for antimony pentasulfide$_{(II)}$ showed prominent peaks corresponding to interplanar spacings of 7.76 and 4.33 A, weak peaks corresponding to interplanar spacings of 3.36, 2.88, 2.51, 2.47, 1.89 and 1.78 A, and in addition, weak peaks corresponding to the interplanar spacings of rhombohedral sulfur (5). The residue after 6 days extraction with carbon disulfide no longer showed the rhombohedral sulfur peaks nor any of the peaks listed above, but instead gave peaks at interplanar spacings of 6.15, 3.48, 3.04, 2.83, 2.75, 1.82 and 1.70 A. The X-ray diffraction pattern reported in the literature for antimony pentasulfide (2) does not match any of the above patterns.

Determination of ^{121}Sb Isomer Shifts. The Mössbauer spectrometer consisted of an Austin Associates S-3 Constant Acceleration Spectrometer Drive used in conjunction with a Nuclear Data ND-180FM 512 Channel Analyzer. The velocity scale was calibrated in terms of the magnetic hyperfine splitting of iron foil. The source was a $\sim$0.15 mc sample of ^{121}Sn (which decays to ^{121}Sb) in the form of SnO_2. The detector was a methane-xenon filled proportional counter, with the window of the single channel analyzer set on the escape peak of the 37 Kev ^{121}Sb gamma ray. Absorbers containing about 10 mg/cm^2 Sb were prepared by diluting the powdered sample 1:15 with powdered polyethylene and loading the diluted samples into sealed lucite holders. Both sample and source were maintained at 80°K. The data from each spectra were fit by a least squares technique to a single Lorentzian peak with an IBM 360/75 computer. Although quadrupole splitting is expected in these compounds, the large natural line width prevented observation of the small splitting.

Results and Discussion

Ruby *et al.* (6) and Bryukhanov *et al.* (7) have reported isomer shifts for several Sb(III) and Sb(V) compounds. Using data from these two sources, the range of isomer shifts (SnO_2(^{121}Sb) source taken as zero) reported for Sb(III) compounds falls between -10.4 and -14.8 mm/sec; for Sb(V) compounds between

+3.7 and -3.5 mm/sec. The isomer shifts for the antimony sulfides are listed in Table II along with the corresponding full width at half maximum. Since the isomer shifts all fall between -12.7 and -14.32 mm/sec, it is immediately apparent that these materials contain only antimony(III).

TABLE II

Isomer Shifts and Full Widths at Half Maximum for the Antimony Sulfides

Antimony Sulfide	I.S.* (mm/sec)	Width (mm/sec)
Stibnite	-14.32 ± 0.11	4.31 ± 0.17
Amorphous Antimony Trisulfide	-12.74 ± 0.17	5.22 ± 0.18
Antimony Pentasulfide$_{(I)}$	-12.27 ± 0.11	5.75 ± 0.37
Antimony Pentasulfide$_{(II)}$	-12.54 ± 0.11	5.73 ± 0.26

*Relative to the $SnO_2(^{121}Sb)$ Source

Three of the four samples contain unextractable sulfur beyond that required for the composition Sb_2S_3. This additional sulfur could be accommodated by modifying the stibnite structure by including a variety of randomly located polysulfide linkages, *e.q.* -S-S-, -S-S-S-, in accord with the stoichiometry. Increased disorder also is indicated in these samples by the peak widths as compared with the width of the stibnite peak. The narrowest peak observed is that for stibnite, which is known to contain two different antimony sites (1). The s electron density of the two different types of Sb nuclei in stibnite is not different enough to give rise to two peaks, but the width of the peak is about twice the predicted minimum peak width, 2.1 ± 0.12 mm/sec (8). In the case of the amorphous antimony trisulfide the peak width increases; the increase is still greater for the two pentasulfides. This increased width may well be due to the large variety of slightly different antimony sites that would be present in a structure made up by randomly incorporating polysulfide linkages between antimony atoms. The difference in isomer shift between the amorphous antimony trisulfide and stibnite is very definitely real and corresponds to a decrease in s electron density at the antimony nucleus in the amorphous material.

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